A/CERRF Proj. # 2835-RG-86/4
Date Received Sept. 3/91
Copy to file ☑ Research Manager ☐
Library ☐ E M & R, Ottawa ☐

Distributed Chemical And Physical Properties of Coal

Research Project 2835-RG-86/4

Final Report

Submitted to the Office of Coal Research and Technology

Alberta Energy

LEGISLATURE LIBRARY
DEC -7 1992
EDMONTON

Sept. 3, 1991
Peter J. Crickmore Ph.D., P.Eng.
Chemical Engineering Department
University of Alberta

TABLE OF CONTENTS

	Page
Executive Summary	1
Appendix A: Fractal geometry, the Korcak law and asphaltene precipitation	5
Appendix B: Prediction of processing performance from two different fractal measures of the distributed attributes of coal	8
Appendix C: Multilayer adsorption on energetically heterogeneous surfaces	14
Appendix D: The fractal geometry of the adsorbate as a measure of energetic heterogeneity	32

EXECUTIVE SUMMARY

Coal consists of a mixture of organic and inorganic chemical species arranged in space in a pattern that is between total randomness and the rigid structure of a crystal. Different "types" of coal are known to have different ranges of chemical species and in physical structures (where "types" is deliberately left vague so that it may refer to different macerals in one sample of coals or to coals of different ranks from different locations). Thus, it may be possible to use some measures of the physical and chemical heterogeneity of a coal as characteristic identifiers. It should be noted at this juncture that this is a departure from the usual predictors used in coal science -- it is usual to use average assays (whether elemental or from proximate analysis or elsewhere) to predict processing behaviour.

Once a decision has been made to use some measures of physical and chemical heterogeneity to characterize coal, the question arises as to which measures to use. Previous work points the direction to follow -- in coal, the heterogeneity tends to cascade over several levels of observation (the relatively homogeneous coal tends to be relatively homogeneous at several scales of observation while the extremely heterogeneous coal tends to exhibit heterogeneity from the maceral level to that of the entire formation. This is suggestive of a fractal distribution of attributes and so it is to fractal geometry and analysis that we will turn for mathematical tools to measure the physical and chemical heterogeneity of the coal. It should be noted that we will not assume that these two measures will always be independent; for instance, anthracite is typically a material with low physical and chemical heterogeneity while lignite should have high measures of both chemical and physical heterogeneity. We will assume that both these variables need to be included for two reasons

- there is evidence from previous work that more than one independent variable is necessary to describe the processing behaviour of coals

- there are some processes in which the behaviour of the coal is more dependent on physical attributes (pore structure for gasification and hardness, etc. for grinding, for

example) while there are others in which the chemical makeup may determine the behaviour (liquefaction for example).

If fractal measures are to be used to model chemical and physical heterogeneity, how should this be accomplished? The modelling of the physical heterogeneity is the easier of the two problems, as the work of other researchers has demonstrated that a surface fractal dimension derived from monolayer capacities of the surfaces of the material for different gases is a good measure of heterogeneity. Materials with smooth surfaces and no pores have fractal dimensions close to two while materials that are both porous and heterogeneous (such as silica gel) have dimensions close to three. Most coals would have fractal dimensions intermediate between these two extremes with lignites tending to have higher fractal dimensions than (for example) anthracites.

There are several possibilities for a fractal dimension that would characterize the chemical heterogeneity of a coal. One approach is to take advantage of the fact that much of the chemical heterogeneity of the coal will be preserved under whatever processing is done. Thus, if a fractal dimension reflecting the diversity of chemical species is established for the product of a coal processing scheme, the fractal dimension may also describe the diversity of chemical species in the parent coal. This approach is taken in "Fractal geometry, the Korcak law and asphaltene precipitation", which is reprinted in Appendix A; in the paper it is clearly demonstrated that a Korcak law describes the species diversity in heavy hydrocarbons such as coal liquefaction products. Presumably, the same conclusion should apply to the parent coal that yielded the coal liquid.

This definition of a fractal dimension to model chemical heterogeneity has (at least) three drawbacks:

- the fractal dimension may be influenced by the process parameters
- the method used must vary with the nature of the products (i.e. asphaltene solubility is probably not a good test for a coal undergoing gasification)
- the focus is not on the coal itself.

These objections can be overcome with the adoption of a fractal dimension based on the energetic heterogeneity for adsorption on the coal's surface. This approach will have the advantage that the same type of experimental investigation that is used for the determination of the fractal dimension describing physical heterogeneity is also used for the chemical fractal dimension.

The paper on "The fractal geometry of the adsorbate as a measure of energetic heterogeneity" (reproduced in Appendix D) indicates how low coverage adsorption data can be used to give a measure of the energetic heterogeneity of the surface of a solid. This energetic heterogeneity is a result of the distribution of chemical species found at the surface of the solid. If we make the assumption that conditions at the surface are representative of conditions throughout the solid (an assumption that we make in using the physical fractal dimension), this measure of energetic heterogeneity for adsorption is a measure of the diversity of chemical species in the solid (coal).

The fractal dimension used to describe the chemical heterogeneity varies from zero (very heterogeneous) to two (homogeneous).

In order to utilize the two measures of heterogeneity, it is helpful to have available an adsorption isotherm for multilayer adsorption over surfaces with varying degrees of energetic heterogeneity. As such an isotherm was not available in closed form, a generalization of the BET isotherm (based on the generalization of the Langmuir isotherm by Crickmore and Wojciechowski) was derived and tested. The paper detailing this new isotherm ("Multilayer adsorption on energetically heterogeneous surfaces) is reproduced in Appendix C.

A short synopsis of this work and its application to coal processing stream is given in Appendix B ("Prediction of processing performance from two different fractal measures of the distributed attributes of coal").

Future work on this project should focus on the use of the tools derived here --- obtaining

suitable adsorption data for a number of gases on a variety of coals for which processing behaviours are known and then examining critically the correlation structure that results.

APPENDIX A

Fractal geometry, the Korcak law and asphaltene precipitation.
P.J. Crickmore and C. Hruska,
FUEL 68, 1488-1489 (1989).

paraffins plus heavily paraffin substituted aromatic compounds, and light aromatics plus phenol substituted aromatic compounds, respectively. The ratio of the first to the second peak decreased as the temperature was increased, i.e. the content of heavily paraffin substituted aromatic compounds decreased as thermal cracking increased. This effect was observed under both He and H_2 atmospheres.

Figure 2 shows the cumulative molecular weight distributions of pyrolysis and hydropyrolysis tars as functions of temperature. To better compare the distribution curves, they have been divided into two areas, one for each of the two peaks described above. At temperatures of $\leq 600°C$, the area of the first peak is remarkably less for hydropyrolysis tars, but at temperatures close to 700°C the difference between the molecular weight distributions decreases. At 500°C the ratio of the first to the second peak is 1.5 (60:40) under He and 0.82 (45:55) under H_2. At 600°C the ratio is 1.22 (55:45) under He and 0.60 (37:63) under H_2, i.e., the ratio at 500°C under H_2 is lower than under He at 600°C. At 700°C the ratios are 0.66 (40:60) under He and 0.43 under H_2.

Consequently, the greatest differences between the molecular weight distributions of pyrolysis and hydropyrolysis tars from a Spanish low rank coal are observed within the temperature range of 500–600°C, which is also the range over which tar yields are maximized[3]. At temperatures close to 700°C the differences in molecular weight distribution are much smaller, although differences in tar yields are still significant. It follows that a hydrogen atmosphere has an influence on molecular weight distribution only if thermal post-cracking is not extensive, since if it is, the main effect of hydrogen is to increase tar yield.

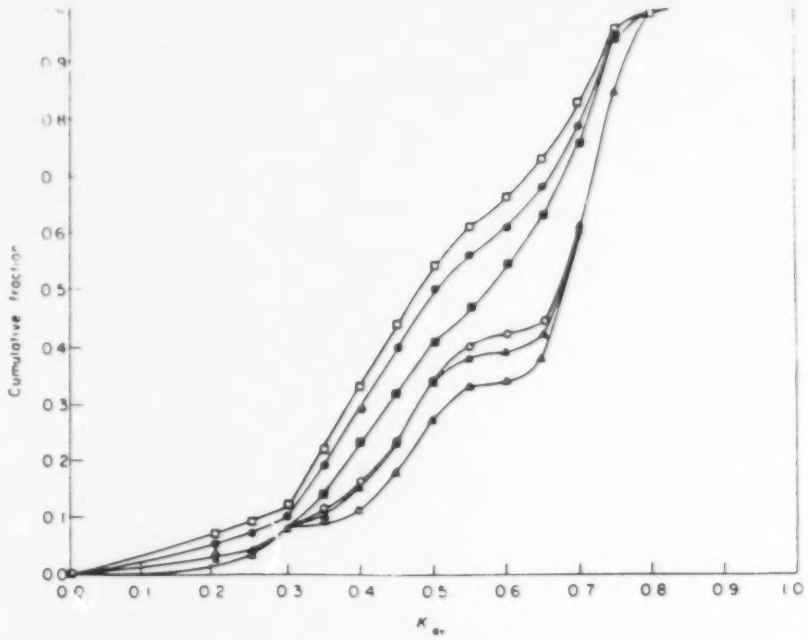


Figure 2 Cumulative distributions of molecular weight for pyrolysis and hydropyrolysis tars as functions of temperature. See *Table 1* for relation between K_{a_n} and $\bar{M}_n$: □, He 500°C; ●, He 600°C; ■, H_2 500°C; ○, He 700°C; ▲, H_2 600°C; △, H_2 700°C

REFERENCES

1 Ladner, W. R. and Snape, C. E. Proc. Int. Conf. on Coal Science, Sydney, Australia, 1985, p. 949

2 Philip, C. V. and Anthony, R. G. *J. Chrom. Sci.* 1986, **24**, 438

3 Cyprès, R. and Moliner, R. *Fuel Proc. Technol.* 1987, **15**, 101

Fractal geometry, the Korćak law and asphaltene precipitation

Peter J. Crickmore and Craig Hruska*

Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada

(Received 7 June 1989, revised 3 July 1989)

This paper presents a method of correlating the solubility of a given heavy hydrocarbon in a light hydrocarbon solvent. The method uses two fractal dimensions – one to describe the size distribution of the heavy hydrocarbon 'particles' (molecules, micelles, aggregates) in solution, and the other to describe the surface irregularity of the particles. Data originally published by Mitchell and Speight fit well with the model. Analysis of Mitchell and Speight's data suggests that differences in solubility of a given heavy hydrocarbon between solvents are mainly dependent on differences in the size distribution of the heavy hydrocarbon particles in solution.

(Keywords: hydrocarbon; solubility; fractal geometry)

Methods of predicting the solubility of heavy hydrocarbons in lighter hydrocarbons have received much attention over a number of years. Factors that have been identified as influencing the solubility of heavy hydrocarbon components are the chemical natures of the heavy hydrocarbon and the lighter hydrocarbon[1,2], the temperature[3,4], the pressure[4], and the nature and extent of the contact between heavy and light hydrocarbons[5]. Correlations of asphaltene precipitation using either of the Hildebrand solubility parameters[1] or a thermodynamic approach[4] based on the Flory–Hildebrand theory have been fairly successful. However, neither correlation can be used to predict the variation in the amount of precipitate with the nature and extent of the contact between the heavy and light hydrocarbons. In addition, the thermodynamic approach requires the assumption of reversible asphaltene precipitation.

This study approaches the problem from a more fundamental viewpoint, by considering the distributions in size and surface geometry of heavy hydrocarbon

* Present address: Gulf Canada Resources, Edmonton, Alberta, Canada

0016-2361/89/111488-02$3.00

© 1989 Butterworth & Co. (Publishers) Ltd

particles (molecules, micelles, aggregates) in solution. Such an approach may also be of use in modelling the viscosity of systems containing heavy hydrocarbons[6, 7] and in modelling the variation of measured molecular weight of heavy hydrocarbons in different solvents[8].

THEORY

Consider as a system, a quantity of solvent with dissolved heavy hydrocarbon species. For most systems there will be a considerable distribution in the size of the heavy hydrocarbon particles (molecules, micelles, aggregates), as a limiting case, we could consider this distribution to follow the Korcak law[9, 10]:

$$N(V>r) = Fr^{-D/3} \tag{1}$$

where the left-hand side represents the number of heavy hydrocarbon particles whose volume (V) exceeds some specified volume (r). In addition, D can be considered a dimension and F a normalizing factor. The value of D may range between zero for a very dilute system and three for an extremely concentrated system. Equation (2) can be used to generate an expression for the total amount of heavy hydrocarbon in solution in the system of interest (m_T):

$$m_T = \frac{FD\rho}{3-D} t_M^{(3-D)/3} \tag{2}$$

where t_M denotes the volume of the largest heavy hydrocarbon particle in solution, and ρ is an average density of heavy hydrocarbon in the particles.

The volume term in Equation (2) is a volume as 'seen' by the molecules of solvent. Following Avnir and Pfeifer[11], t_M can be rewritten as

$$t_M = k' L^{D^*} \tag{3}$$

where D^* is a dimension corresponding to the surface irregularity of the largest heavy hydrocarbon particle in solution, and L is a characteristic length of the solvent molecule (to be consistent, we will take L to be the greatest diameter of the solvent molecule). The value of D^* can vary from 1 or 2 for a smooth surface to 3 for a very irregular surface. Combining Equations (2) and (3) results in:

$$m_T = \frac{kFD\rho}{3-D} L^{D^*(3-D)/3} \tag{4}$$

where

$$k = (k')^{(3-D)/3} \tag{5}$$

COMPARISON WITH DATA

Figures 1, *2* and *3* test Equation (4) with data from Mitchell and Speight[1] (for solubilities of one bitumen in different solvents) and Bondi[12] (for the dimensions of the solvent molecules). m_T is measured in g heavy hydrocarbon per mole solvent, and L is in nm. The agreement between the data and Equation (4) is excellent. The best-fit slopes and intercepts from the three curves indicate that at least D (and possibly D^* as well) changes with solvent class for a fixed heavy hydrocarbon (see *Table 1*). Unfortunately, solubility data is not sufficient to specify both D and D^*; measurements of other properties (such as the average molecular weight of the heavy hydrocarbons in solution, or the viscosity of the mixture) would be required in conjunction with the present analysis to pinpoint both dimensions. However, if we assume that kF is constant for all solvent types studied here, D increases as we change from 1-alkenes to n-alkanes to iso-alkanes. This increase in D is sufficient to account for the variation in D^* ($3-D$)/3, so that D^* would vary little for the three solvent types considered here.

Once we have assumed that the Korcak law adequately describes the size distribution, the distribution is totally specified by the size of the largest particle that remains in solution. This leads to a question - are the smallest particles that come out of solution described by the same distribution law? If they are, then it may be possible to propose structures for the asphaltenes that precipitate from solution based on properties of the heavy hydrocarbons that remain in solution (D and D^*).

Table 1 Parameter values for different solvent classes

Solvent type	$kF D\rho/(3-D)$	$D^*(3-D)/3$
n-Alkanes	1.74	0.941
1-Alkenes	1.64	0.983
iso-Alkanes	2.37	0.74

ACKNOWLEDGEMENT

This research was partially funded by a grant-in-aid of research from the Alberta Canada Energy Resources Research Fund, jointly established by the Governments of Alberta and Canada, and administered by the Alberta Office of Coal Research and Technology.

REFERENCES

1. Mitchell, D. M. and Speight, J. G. *Fuel* 1973, **52**, 149
2. Peluso, M. and Ogrew, D. F. *Chem. Eng. Progress* 1979, 41
3. Ali, L. H. and Al-Ghannam, K. A. *Fuel* 1981, **60**, 1043
4. Hirschberg, A., deJong, L. N. J., Schipper, B. A. and Meijer, J. G. *Soc. Petrol. Eng. J.* 1984, **24**(3), 283
5. Speight, J. G., Long, R. B. and Trowbridge, T. D. *Fuel* 1984, **63**, 617
6. Khan, M. A. B., Mehrotra, A. K. and Svrcek, W. Y. *J. Can. Petrol. Tech.* 1984, 47
7. Christensen, R. J., Lindberg, W. R. and Dorrence, S. M. *Fuel* 1984, **63**, 1312
8. Moschopedis, S. E., Fryer, J. F. and Speight, J. G. *Fuel* 1976, **55**, 227
9. Korčak, J. *Bull. Inst. Int. Stat. III* 1983, 295
10. Mandelbrot, B. B. in 'The Fractal Geometry of Nature', Freeman, San Francisco, USA, 1982, p. 117
11. Avnir, D. and Pfeifer, P. *Nouveau J. Chim.* 1983, **7**, 71
12. Bondi, A. in 'Physical Properties of Molecular Crystals, Liquids and Glasses', John Wiley & Sons, New York, USA, 1968, p. 453

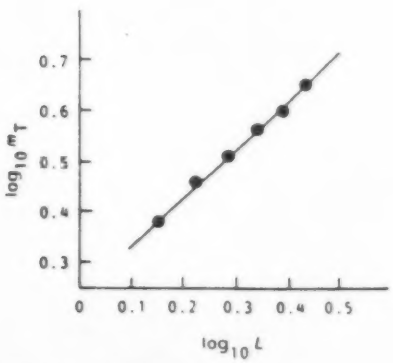


Figure 1 Solubility in n-alkanes

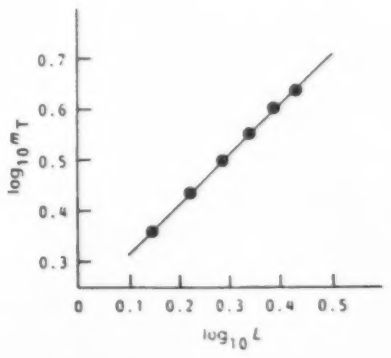


Figure 2 Solubility in 1-alkenes

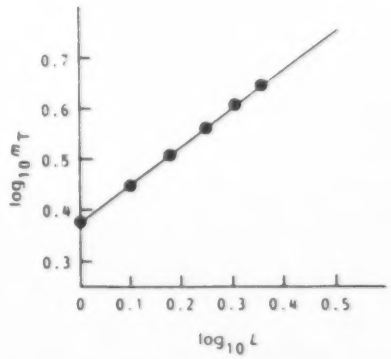


Figure 3 Solubility in iso-alkanes

APPENDIX B

Prediction of processing performance from two different fractal measures of the distributed attributes of coal.
Peter J. Crickmore
OCRT Symposium on Coal Research, Calgary, 1990, pp 3-7

PREDICTION OF PROCESSING PERFORMANCE FROM TWO DIFFERENT FRACTAL MEASURES OF THE DISTRIBUTED ATTRIBUTES OF COAL

Peter J. Crickmore
Department of Chemical Engineering
University of Alberta
Edmonton, Alberta T6G 2G6
(403) 492-3472

Introduction Prediction of the "processibility" of a particular coal (here"processibility" means performance as a gasification, liquefaction, pyrolysis, grinding, combustion or other process feedstock) is typically made through correlations based on rank, proximate analysis, or elemental assays (e.g.(1)). The problem with such correlations is that they are not very good; the precision of most estimates is poor. The difficulty with these correlations lies not with any systematic lack of fit but with the unavoidable heterogeneity of the coal; it is impossible to guarantee that the samples of coal that are used for the assays are identical in all respects to the samples used for assessing the processibility behaviour. Even if it were possible to homogenize a sample of coal to such an extent that subsampling could be done without error, the resulting correlation would not be of much use in predicting the processibility of a "real" coal. It can be shown (2) that the processibility behaviour of a mined material that possesses natural spatial segregation is quite different from the processibility behaviour of the same material when processed in exhaustively

homogenized batches. "Real" coals, such as would be encountered in the feed to a pilot unit or a commercial plant will exhibit heterogeneities or spatial segregation effects on all scales from within-maceral variability to long term trends in coal characteristics over the life of a mined deposit.

A different approach to characterizing coal is to try to focus on those attributes that make coal coal; what is it about coal that differentiates it from an equivalent amount of graphite, elemental sulphur, water and inorganic salts? It seems likely that the most characteristic thing about coal is its chemical and physical heterogeneity on all scales; in addition, the nature of the heterogeneity should vary from coal to coal (it seems obvious that the heterogeneity in lignite is different from the heterogeneity in anthracite).

How should such chemical and physical heterogeneity be modelled? Current research suggests that fractal geometry could be used to model the heterogeneity in such a way that a measure that is characteristic of the processes that formed the coal (previous studies of mineral deposits have demonstrated that fractal analysis will pinpoint deposits that have arisen by pure sedimentation (3) and by diffusive displacement (4)).

We shall examine, in turn, fractal dimensions that will characterize the physical and the chemical heterogeneity of

coal.

Characterization of the Physical Heterogeneity of Coal Coal possesses obvious manifestations of physical heterogeneity: porosity is evident over a wide range of pore sizes, fracture surfaces of coal vary in complexity and plant remains in varying stages of alteration along with inclusions of inorganic matter may be present. Any of these manifestations of heterogeneity could be chosen as representative of the heterogeneity of coal; the most general choice appears to be the range of porosity across different scales as all coals will exhibit some degree of porosity.

The problem of characterizing how the porosity of a solid varies across different length scales (or, alternatively, how irregular the surface of the solid is) has been addressed by Avnir and Pfeiffer (5). They considered how the surface area of a solid, as measured by physical adsorption of a vapour, changes with the size of the molecule that adsorbs. Their analysis led to

$$A \propto \sigma^{(2-D)/2} \qquad 1.$$

where A is the measured surface area, σ is the surface area of a single molecule adsorbed on the surface and D is the fractal dimension of the surface of the solid. D will vary

between 2 for extremely smooth surfaces and 3 for extremely irregular surfaces; values for coal fall into the range from 2.2 to 2.6.

Characterization of the Chemical Heterogeneity of Coal In addition to the physical heterogeneity, chemical species in coal possess a marked spatial segregation. Some of this is obvious, such as the appearance of pyrite crystals or layers of silicates. Some of the chemical heterogeneity, however, exists on the molecular level and is the major reason why answers to questions such as "What is the molecular structure of coal?" are not forthcoming.

If we are willing to make the assumption that any chemical heterogeneity of coal will be manifest throughout the coal, we can restrict our investigation to the surface of the coal and ask if there are any experimental probes that would determine chemical segregation effects there. One such approach is to use the approach of Crickmore and Larson (6) and examine the fractal dimension of adsorbed species at low relative coverage (D_s) as a measure of the energetic or chemical segregation on the surface. D_s should vary between 0 for extremely heterogeneous surfaces and 2 for completely homogeneous surfaces. Values for adsorption of alcohols on Kentucky No. 12 coal (bituminous A) range from 0.2 to 0.5 indicating that bituminous coal is a reasonably heterogeneous

material; this numerical measure seems to be a good reflection of what we feel we already know about the chemical heterogeneity of coal.

Discussion on the Use of D and D_s as Characterization Parameters for Coal Ongoing work is underway to use the two parameters identified above as independent variables in correlations to predict "processibility" performance. In particular, since D is based upon the geometry that controls diffusion rates and D_s is based upon energetics that may enter into reaction rates, the two fractal dimensions may be very useful in modelling processes that depend on a combination of mass transfer and chemical reaction.

REFERENCES

1. Several reviews of this material are available: the most complete would appear to be Berkowitz, N., The Chemistry of Coal, Elsevier, Amsterdam, 1985.
2. Crickmore, P.J., Schutte, R., and Cleaver, J.A.S., AOSTRA J. Research 5, 195 (1989).
3. Mandelbrot, B.B., and Wallis, J.R., Water Resources Research 5, 321 (1969).
4. Shaw, R.C., Crickmore, P.J., and Kratochvil, B., Applications of Fractal Geometry to Oil Sand Sampling, 38th CSChE Conference, Edmonton, 1988.
5. Avnir, D. and Pfeiffer, P. Nouveau J. Chim. 7 71 (1983).
6. Crickmore, P.J. and Larson, B.S., The Fractal Geometry of the Adsorbate as a Measure of Energetic Heterogeneity, 72nd Can. Chem. Conf., Victoria, 1989.

APPENDIX C

Multilayer Adsorption on Energetically Heterogeneous Surfaces
Peter J. Crickmore and Bret S. Larson
72nd Canadian Chemical Conference, Victoria, June 1989.

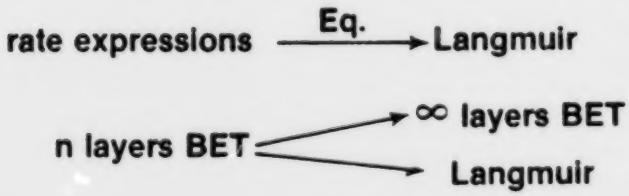
Multilayer Adsorption on Energetically Heterogeneous Surfaces

P.J. Crickmore and B.S. Larson

Department of Chemical Engineering
University of Alberta

Strengths

- simple equations
- physical model(s)
- limiting process leads from one form to another



Weaknesses

- no rate law
- choice of local isotherm and distribution function uncertain
- cumbersome to use (unless a closed form solution exists)

Another Approach:
(Crickmore and Wojciechowski, 1977)

- for an arbitrary rate constant distribution for adsorption

$$r_{ads} \simeq \overline{k}_a N_o (1-\theta)^{1+W_p}$$

$\overline{k}_a$ = mean of the red for adsorption

$W = \sigma/\overline{k}_a$

Similarly, for desorption

$$r_d = \overline{k}_d N_o \theta^{1+W}$$

At equilibrium,

$$\theta = \frac{(Kp)^{1/1+W}}{1 + (Kp)^{1/1+W}}$$

which has been successful in fitting many sub-monolayer systems

Multilayer Adsorption?

- assume Crickmore-Wojciechowski isotherm describes 1st layer
- occupied sites in nth layer provide only possible sites for adsorption in (n+1)st layer
- BET development used for counting adsorbed molecules

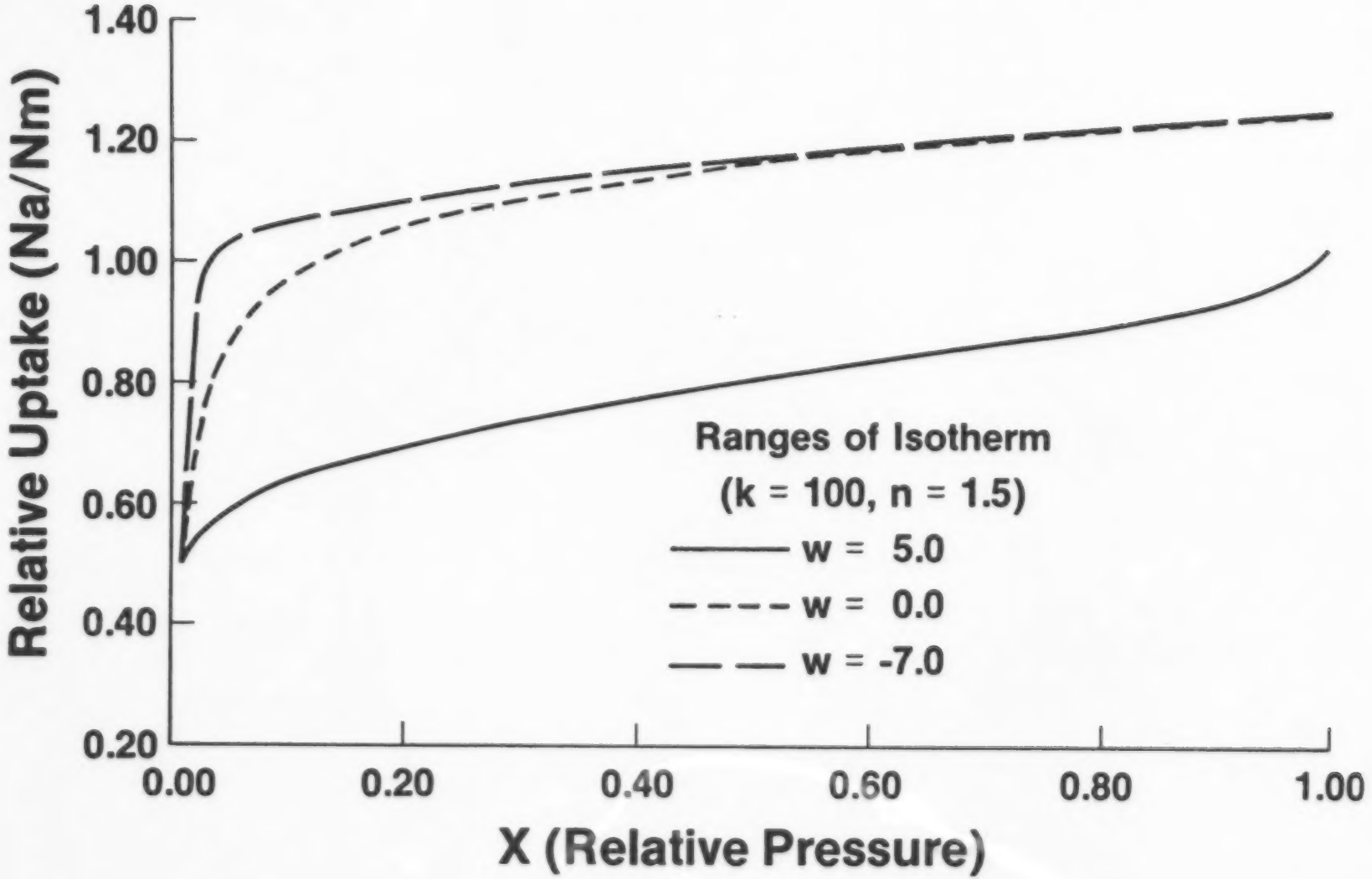
$$\frac{N}{N_0} = \frac{\theta_1}{1 - x} \left\{ \frac{nx^{n+1} - (n+1)x^n + 1}{1 - x^n} \right\}$$

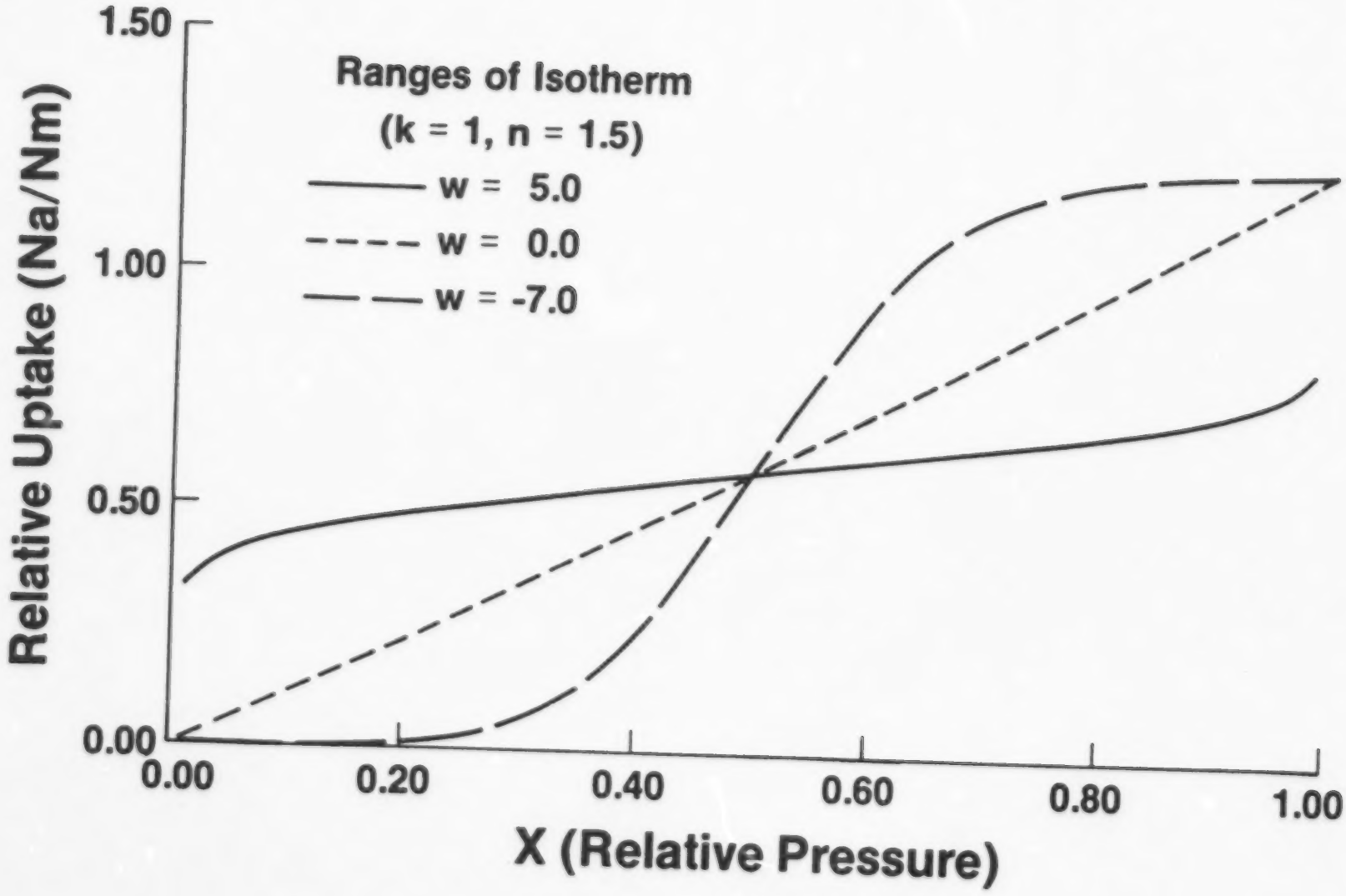
where

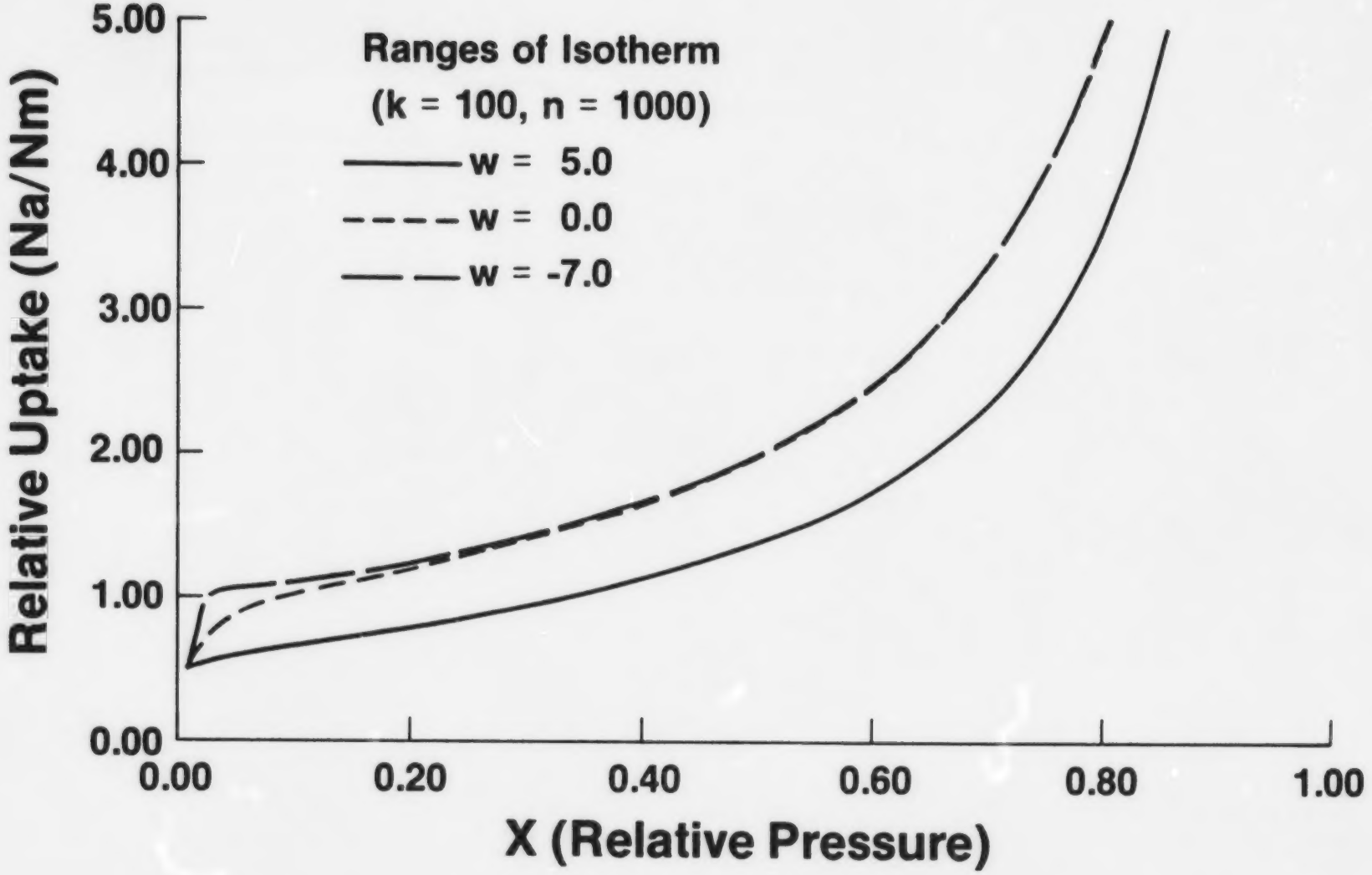
$$\theta_1 = \frac{(Kg)^{1/1+W}}{1 + (Kg)^{1/1+W}}$$

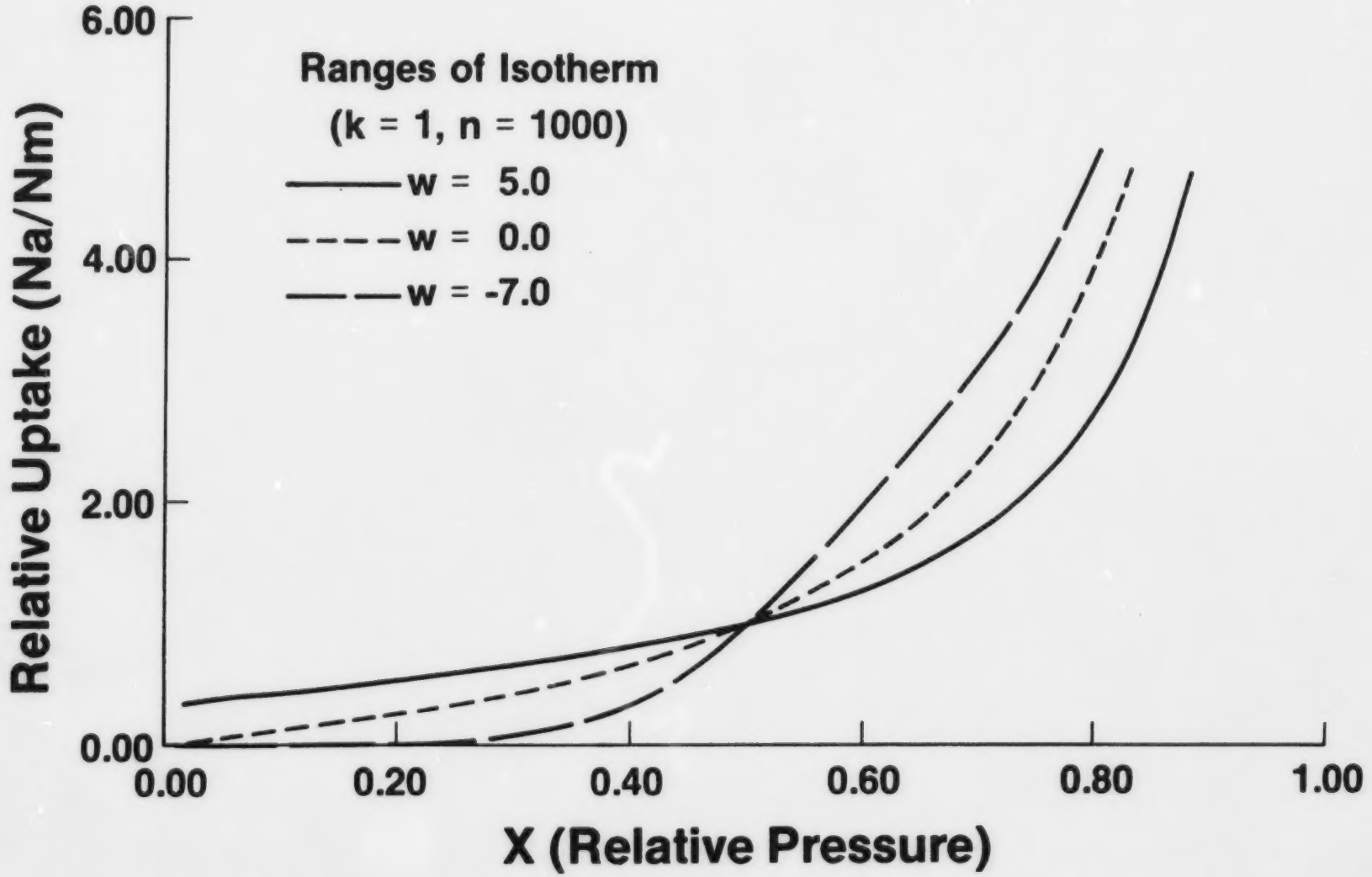
and

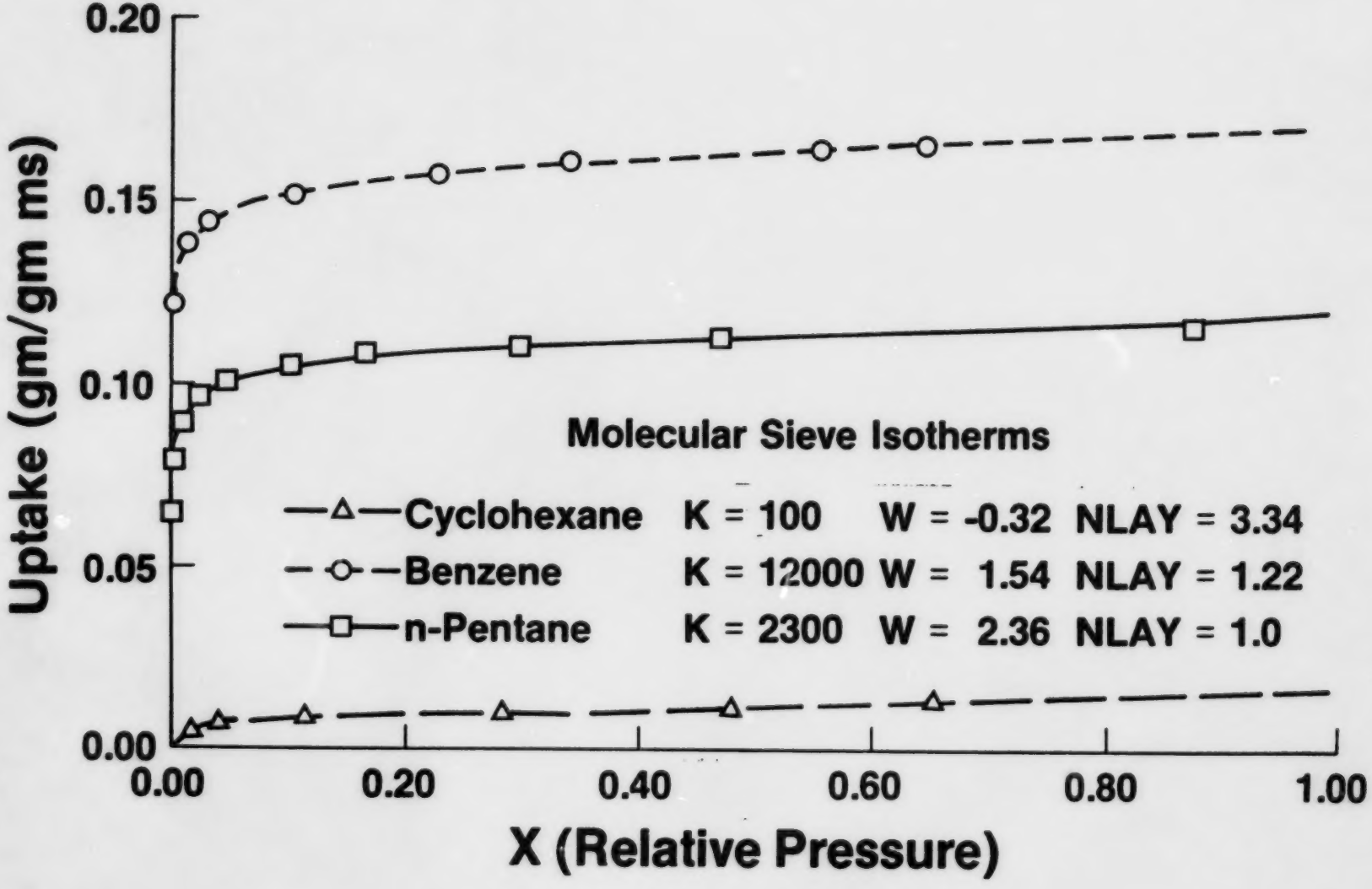
$$g = \frac{x}{1 - x}$$

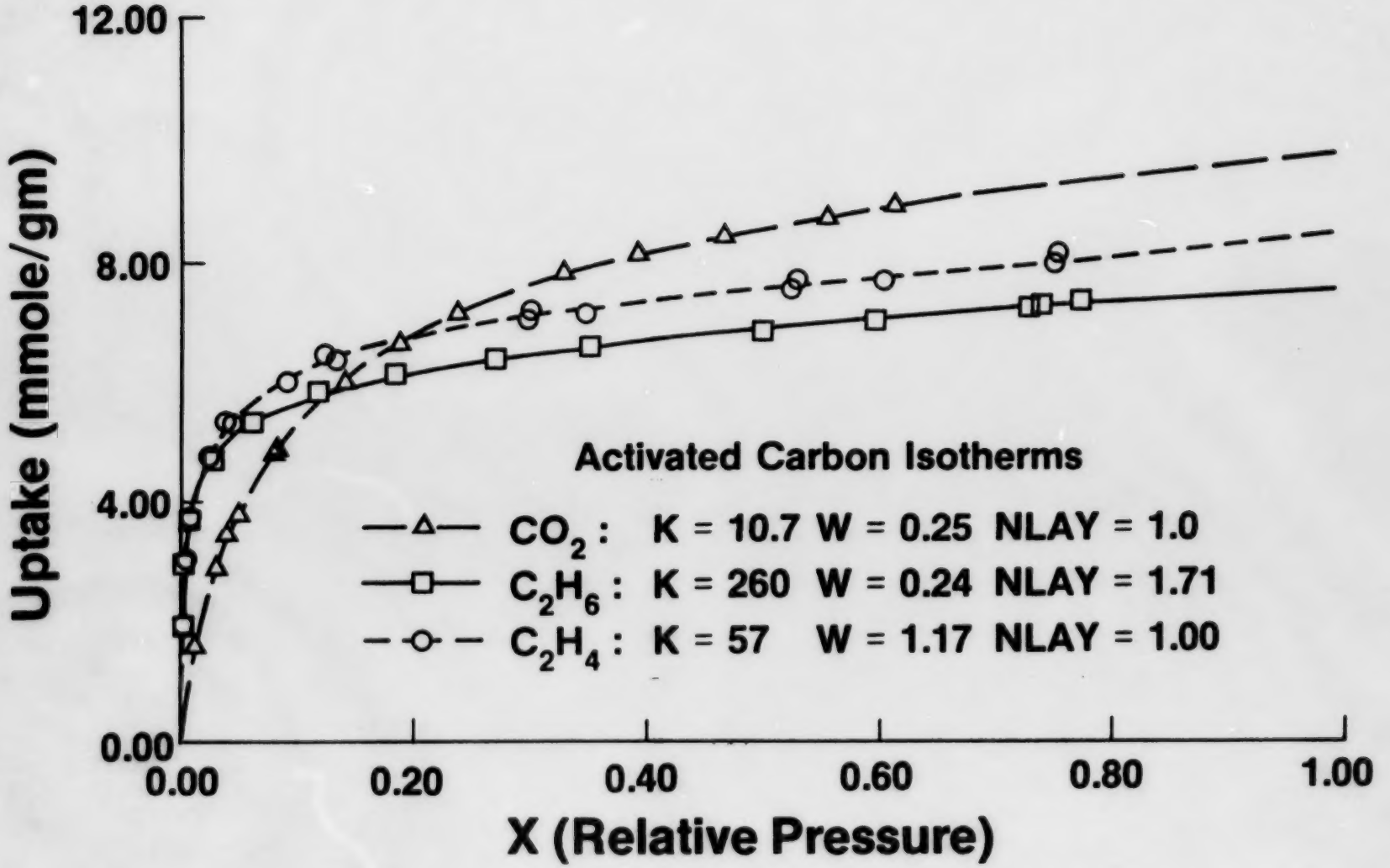

1.40
1.20
1.00
0.80
0.60
0.40
0.20
Relative Uptake (Na/Nm)
Ranges of Isotherm
(k = 100, n = 1.5)
w = 5.0
w = 0.0
w = -7.0
0.00
0.20
0.40
0.60
0.80
1.00
X (Relative Pressure)

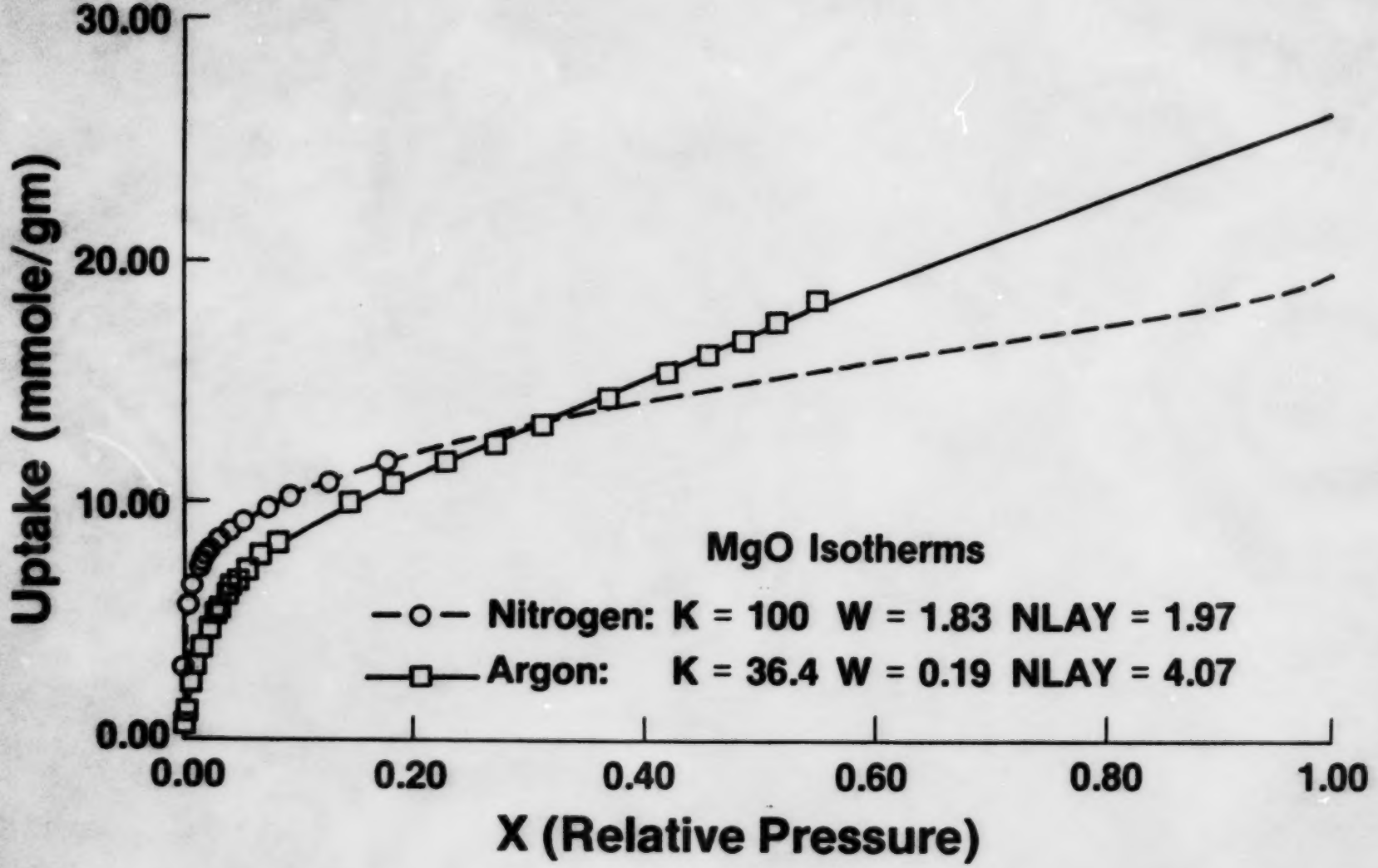

Ranges of Isotherm
(k = 1, n = 1.5)
w = 5.0
w = 0.0
w = -7.0
Relative Uptake (Na/Nm)
1.50
1.00
0.50
0.00
0.00
0.20
0.40
0.60
0.80
1.00
X (Relative Pressure)

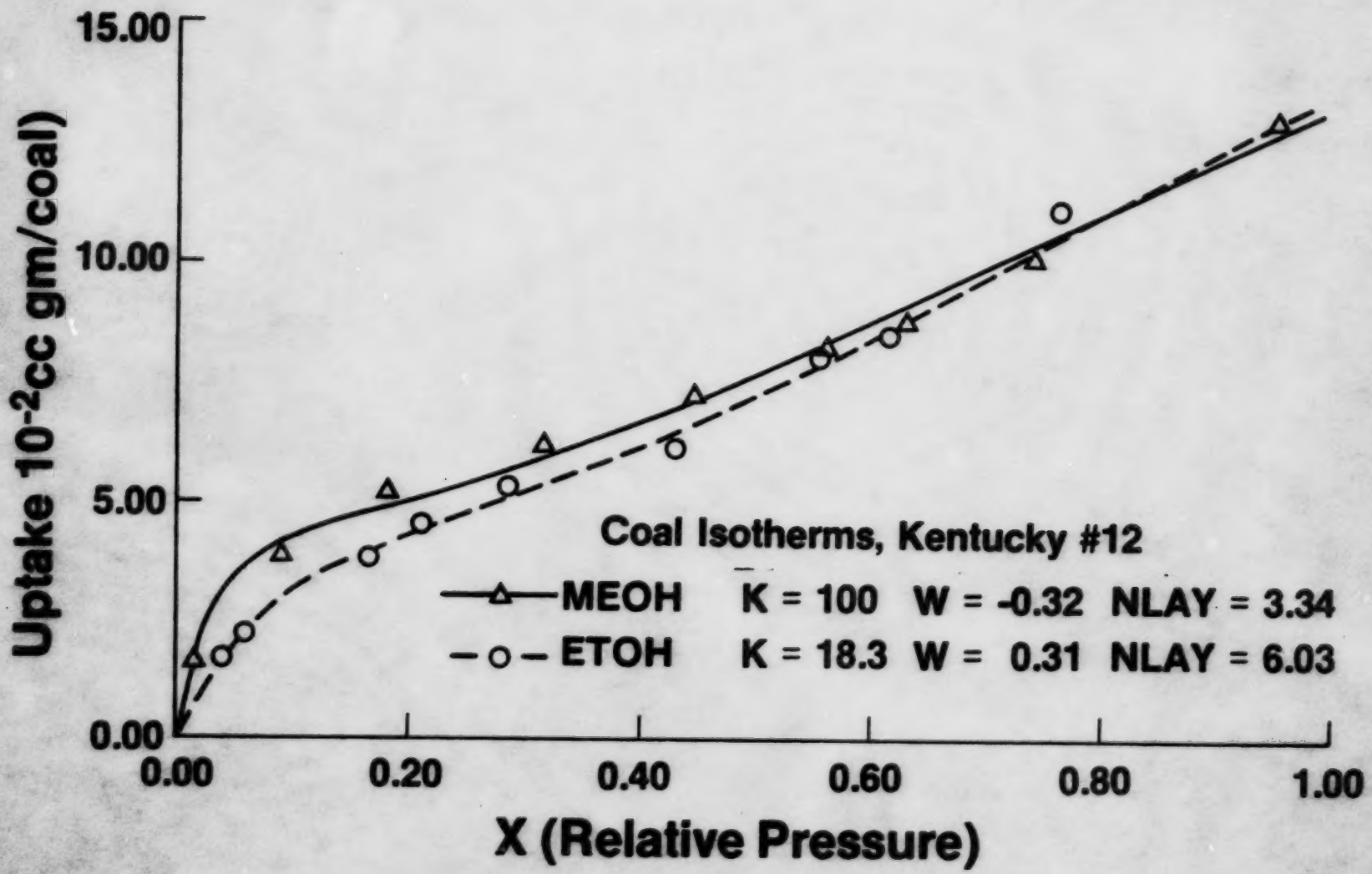

Ranges of Isotherm
(k = 100, n = 1000)
w = 5.0
w = 0.0
w = -7.0
Relative Uptake (Na/Nm)
5.00
4.00
3.00
2.00
1.00
0.00
0.00
0.20
0.40
0.60
0.80
1.00
X (Relative Pressure)


Ranges of Isotherm
(k = 1, n = 1000)
w = 5.0
w = 0.0
w = -7.0
Relative Uptake (Na/Nm)
6.00
4.00
2.00
0.00
0.00
0.20
0.40
0.60
0.80
1.00
X (Relative Pressure)


0.20
0.15
0.10
0.05
0.00
Uptake (gm/gm ms)
Molecular Sieve Isotherms
Cyclohexane K = 100 W = -0.32 NLAY = 3.34
Benzene K = 12000 W = 1.54 NLAY = 1.22
n-Pentane K = 2300 W = 2.36 NLAY = 1.0
0.00
0.20
0.40
0.60
0.80
1.00
X (Relative Pressure)


12.00
8.00
4.00
0.00
Uptake (mmole/gm)
0.00
0.20
0.40
0.60
0.80
1.00
X (Relative Pressure)
Activated Carbon Isotherms
CO2 : K = 10.7 W = 0.25 NLAY = 1.0
C2H6 : K = 260 W = 0.24 NLAY = 1.71
C2H4 : K = 57 W = 1.17 NLAY = 1.00


30.00
20.00
10.00
0.00
Uptake (mmole/gm)
MgO Isotherms
Nitrogen: K = 100 W = 1.83 NLAY = 1.97
Argon: K = 36.4 W = 0.19 NLAY = 4.07
0.00
0.20
0.40
0.60
0.80
1.00
X (Relative Pressure)


15.00
10.00
5.00
0.00
Uptake 10^{-2}cc gm/coal)
0.00
0.20
0.40
0.60
0.80
1.00
X (Relative Pressure)
Coal Isotherms, Kentucky #12
MEOH K = 100 W = -0.32 NLAY = 3.34
ETOH K = 18.3 W = 0.31 NLAY = 6.03

Conclusions

- have a four parameter model for multilayer adsorption on heterogeneous surfaces
- can calculate fractional coverage in each layer
- parameters have physical meaning
- more accurate determination of specific surface area.

Acknowledgement

This research was partially funded
by a grant-in-aid of research from the
Alberta/Canada Energy Resources Research Fund.

APPENDIX D

The Fractal Geometry of the Adsorbate as a Measure of Energetic Heterogeneity
Peter J. Crickmore and Bret S. Larson
72nd Canadian Chemical Conference, Victoria, June 1989.

The Fractal Geometry of the Adsorbate as a Measure of Energetic Heterogeneity

P.J. Crickmore and B.S. Larson

Department of Chemical Engineering
University of Alberta

Heterogeneity of Adsorbents and Catalysts

- irregular surfaces
- pore size distribution
- energetic heterogeneity

Fractional geometry can characterize irregularity or heterogeneity.

Pore Size Distribution

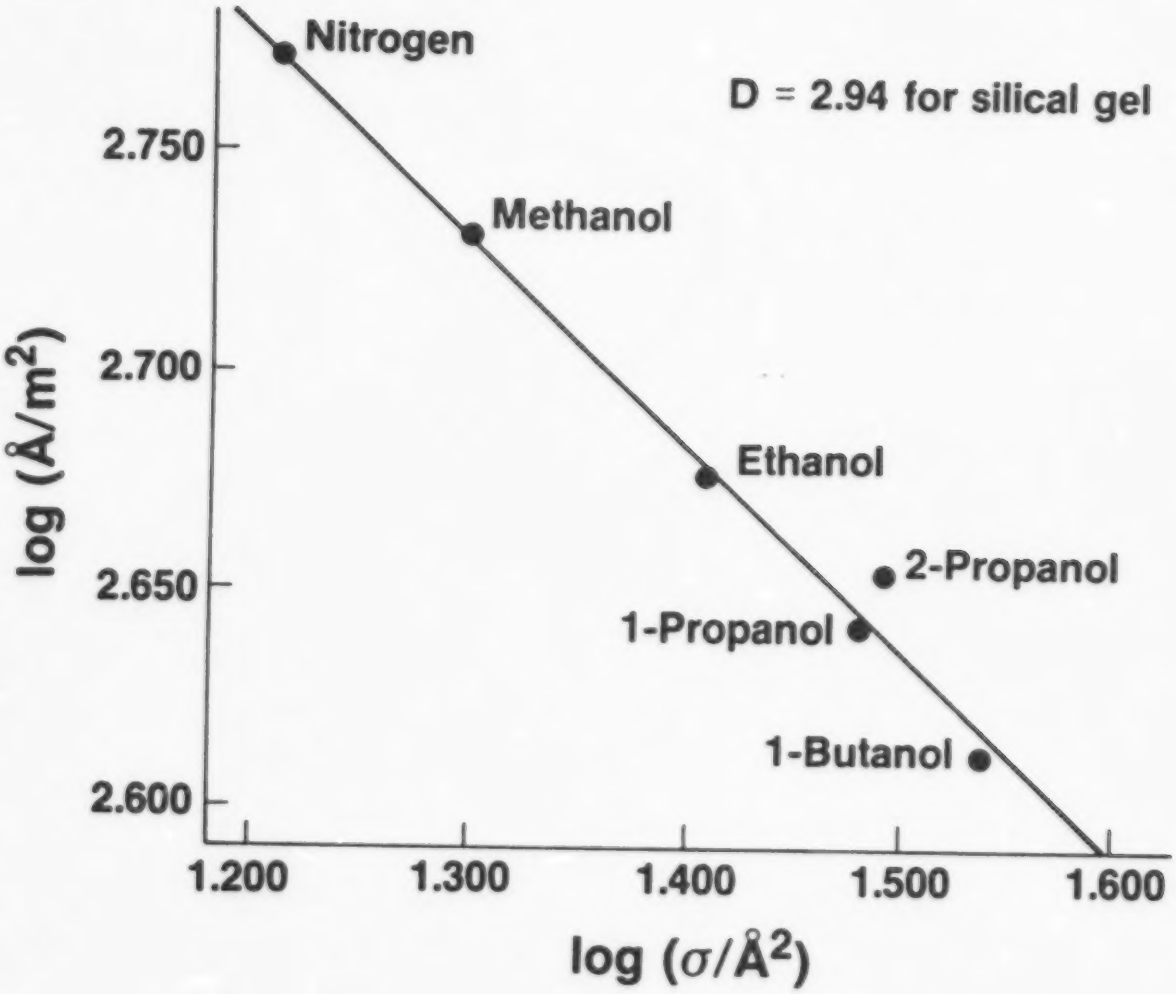
- wide pore mouths → pores are part of the irregular surface
- narrow pore mouths (hysteresis) → no good results yet

Irregular Surfaces

- smaller adsorbates "see" a larger surface area:

$$A \propto \sigma^{(2-D)/2}$$

$$2 \leq D \leq 3$$



Avnir and Pfeifer (1983)

Energetic Heterogeneity

- induces spatial segregation of adsorbed species
- strong influence on (at least some) catalytic reaction rates
- may be linked to overall chemical heterogeneity of adsorbent.

How to Model?

- isolate the surface on which adsorption occurs
- stretch and deform the surface into a 2 dimensional object of area S^*
- consider the mass adsorbed onto S^*

How to Model?

$$M = k\, S^{D_a/2}$$

S = the convex hull of the adsorbed species
$\simeq S^*$ for all but infinitesimal coverages

D_a varies from 0 at low coverages to
2 when the monolayer is complete

How to Evaluate?

- for all systems, D_a=2 at monolayer completion → evaluate k at this point
- can then evaluate D_a at any coverage less than this
- to compare different systems, should evaluate at the same coverage

In practice:

- assume D_a=2 when θ=0.95.
  Record x at this point and calculate k
- evaluate mass adsorbed at x′=0.01 x
  and calculate D_a

Adsorbent	Adsorbate	D_a
Active Carbon	Ethane	1.72
Active Carbon	CO_2	1.45
Active Carbon	Ethylene	1.77
Zeolite L	n-Pentane	1.89
Zeolite L	Benzene	1.92
Zeolite L	Cyclohexane	0.22

Adsorbent	Adsorbate	D_a
MgO	Argon	0.07
MgO	Nitrogen	1.21
Coal	MeOH	0.58
Coal	EtOH	0.24

Discussion

- results are independent of isotherm, but a good isotherm is necessary to handle data
- together with Avnir and Pfeifer's work, may explain "reactive fractal dimensions" greater than 3
- may be correlated with bulk chemical heterogeneity (e.g. coal)

Acknowledgement

This research was partially funded
by a grant-in-aid of research from the
Alberta/Canada Energy Resources Research Fund.